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M. Christensen, A. Dawson, D. Demonbrun and R. Vanholden
Oceaneering Space Systems

P. M. Holland
Thorleaf Research

B. J. Shortt
EADS Astirum Ltd., UK

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ABSTRACT

Progress on the delivery of the Vehicle Cabin Atmosphere Monitor (VCAM) is reported. VCAM is an autonomous trace-species detector to be used aboard the International Space Station (ISS) for atmospheric analysis. The instrument is based on a low-mass, low-power miniature preconcentrator, gas chromatograph, and Paul ion trap mass spectrometer (PCGC/MS) capable of measuring volatile constituents in a space vehicle or planetary outpost at sub-ppm levels. VCAM detects and quantifies 40 target compounds at their 180-day Spacecraft Maximum Allowable Concentration (SMAC) levels. It is designed to operate autonomously, maintenance-free, with a self-contained carrier and calibration gas supplies sufficient for a one-year lifetime. Two flight units will be delivered for operation in the ISS EXPRESS rack.

INTRODUCTION

Long duration human flight (LDHF) can pose severe health risks to astronauts. Mitigating harmful chemical exposure requires a sensitive monitoring instrument as part of a spacecraft life-support system. The planned list of LDHF initiatives involving ISS, Orion, Lunar Outpost and Mars missions requires that the monitoring instrument be relevant with regard to sensitivity, chemical targets, mass range, resolution, and instrument mass-volume-power. Examination of the chemicals on the SMAC target list shows the analytical difficulty of the task. Given the variety and concentrations of these chemicals, coupled with the potential for unexpected and unknown chemical releases into the LDHF environment, a gas chromatograph mass spectrometer (GC/MS) is the best instrument to address these requirements. It is the standard instrument for analysis of chemicals in terrestrial and planetary environments. GC/MSs have successfully flown on unmanned planetary missions such as Pioneer Venus, Galileo, and Cassini, with comparable instruments to be proposed to Venus, Saturn and Titan. A description of the VCAM GC/MS approach was presented earlier [1-4]. New results are presented here on the current state of VCAMs analytical performance, and progress made in delivering VCAM to flight. Included are the VCAM concept of operations, and test results for identification and quantification of the complex gas mixtures expected aboard the ISS.

THE VCAM FLIGHT INSTRUMENT

A schematic diagram of the VCAM layout is shown in Fig. 1, and a 3-D CAD illustration is given in Fig. 2. Air from the astronaut environment

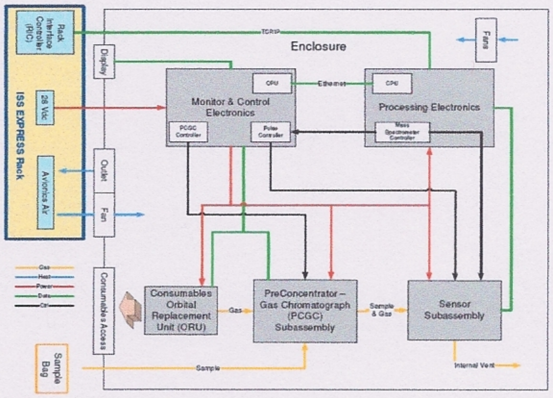

Figure 1. Schematic Presentation of the VCAM Subassemblies. The Paul ion trap is contained in the vacuum Sensor Subassembly Module; the calibration and He carrier gases are part of the Consumables ORU.

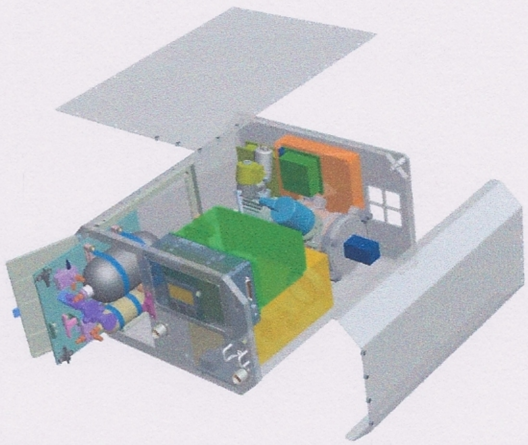

Figure 2. 3D CAD Illustration of VCAM. Exterior panels have been displaced to expose the interior sub-assemblies.

is sampled through a filtered inlet and adsorbed onto a preconcentrator (PC) module. The air is sampled at the VCAM location (typical), but is also introduced through a sample bag filled at other desired locations within the ISS. After adsorption of the volatile organic compounds (VOCs) onto the PC bed the residual air is purged and VOCs are thermally desorbed in a low flow of helium that is directed through the GC microinjector. At the peak of the chemical thermal-desorption profile the microinjector captures approximately $20\mu\ell$ of the stream into the sample loop. This portion is compressed by the pressure of the GC carrier gas, and is injected onto the head of the GC column. The GC elution stream is directed into the center of a Paul ion-trap mass spectrometer. There, a pulsed beam of electrons ionizes the analytes. The resultant ions are then mass-analyzed by the Paul trap in its so-called selective mass-instability mode: the *RF* amplitude is swept linearly in time, and the ionized species are "walked" off the edge of the Paul trap stability region. The mass/charge-selected ions are ejected onto the front cone of a channel-type electron multiplier, and the mass spectrum stored [3]. In the initial testing of the Paul trap it was found that after approximately two month's operation the system lost sensitivity to oxygen-bearing species such as acetone and alcohols. The problem was traced to surface contamination in the Paul trap arising from O-ring breakdown in the GC solenoidal valves. Normal operation was obtained by running the valves at a lower holding current, and by coating the Paul trap electrodes with an inert silanizing layer. Also, an internal halogen bulb maintains the mass spectrometer at approximately 100C during operation to maintain surface cleanliness.

The PCGC, microinjector, heaters, valves, sample pump, and Paul trap sequencing is controlled by the onboard Monitor and Control Electronics (MCE) and Processor Electronics (PE). The mass spectra are analyzed either autonomously onboard, or the data transmitted to ground. In addition, a separate operating cycle—the Major Constituents Analysis—mode is configured for the PCGC/MS. Here, cabin air is introduced directly through the microinjector into the Paul trap through narrow-bore tubing, bypassing the PC and the GC column. In this mode three of the major cabin-air constituents (N_2, O_2, and CO_2) are identified and monitored.

Future developments for VCAM are directed along two paths. The first is to include water-quality monitoring by addition of a water-extraction subassembly that takes advantage of VCAM's modular design. Samples of the habitat's potable water stream are passed over a carboxen preconcentrator bed and the dissolved VOCs are extracted. After several cycles of removing the excess water in a flow of dry He, one heats the PC bed and carries the VOCs in a stream of He onto the microinjector, and thence onto the GC column and into the MS. This subassembly has been tested in the laboratory. It is awaiting integration into VCAM for future use. The second path is to continue the development towards subassemblies having yet lower mass, volume and power. Electronics developments include miniaturization of conventional power supplies to chip size; miniaturization of the *RF* NCO electronics card to chip size; and use of carbon nanotube arrays to effect ionization of the analytes in the trap.

A photograph of the VCAM Development Unit (DU) is shown in Fig. 3. Its mass is 25.2 kg (without consumables) and consumes 140 W (peak) and 100W (nominal) power as derived from the EXPRESS 28V rack. Gas consumables sufficient for one year of operational life are packaged into a separate orbital replacement unit (ORU). Its mass is 5.1 kg. The consumable gases are contained in two tanks: one of pure helium used

Figure 3. Photograph of the VCAM Development Unit (DU). The DU is form, fit, and function of the flight VCAM units and is used for engineering and chemical-detection testing. Its dimensions are 18.1" (width) × 10.8" (height) × 20.5" (depth).

as the GC carrier gas, and the other a calibrant gas mixture. The calibrant is a ten parts-per-million mixture of acetone and fluorobenzene in helium. This mixture enables VCAM to autonomously calibrate the PCGC/MS sub-assemblies on-orbit. Cooling is by means of forced air supplied from the ISS Avionics air-cooling loop; circulation through the VCAM interior by a pair of internal fans. Note that the VCAM sub-assemblies and packaging have not been optimized for volume as they occupy the standard 64.4 liter EXPRESS rack module. Downlink data communication is through the ISS medium-rate data link, buffered onto the ISS high-rate outage recorder and telemetered to Earth. The data are routed through the White Sands and Huntsville Operations Support Center (HOSC), and then through the internet to JPL where they are presented *via* the Telescience Research Kit (TReK). Uplink for on-orbit commanding is along the inverse path.

For laboratory science performance testing two VCAM assemblies are employed, the DU and a separate PCGC/MS called the Laboratory Standard (LS). The LS unit has flight function, and is packaged in an open architecture. On the DU, LS, and Protoflight Units an extensive series of tests are/will be carried out. These consist of establishing, for each target SMAC species a library of GC elution times and MS fractionation patterns. The MS fractionation-pattern library is similar to that of the NIST [5]. The libraries that fly with each system will have been validated to provide accurate identifications and quantification for that instrument. Sample bags each containing mixtures ("cocktails") of 8-10 species at concentrations over the required SMAC limit are prepared and analyzed by the VCAM LS and DU. Also, canisters containing mixtures of SMAC target species, as well as chemicals not on the SMAC list, are supplied to JPL by the JSC analytical laboratory. Verification testing will include varying the total canister pressure over the range 580-830 torr to simulate ISS pressure, and variations in relative humidity. The autonomous identifications and quantifications will be compared with human interpretations of the VCAM raw data; and in the case of JSC-supplied samples with results from the JSC GC/MS instruments. All results will be logged and analyzed. The two Protoflight Units are scheduled for delivery to Kennedy Space Center in 11/08 and 4/09.

PERFORMANCE RESULTS

The target species that appear on the SMAC list are divided into three priority classes: Priority 1 species (nine total) include ethanol, acetone, dichloromethane, and perfluoropropane; Priority 2 (16 total) include benzene, C5-C8 alkanes and C3-C8 aldehydes; and Priority 3 (12 total) include 2-butanone, freon-11, and freon-12. Required detection limits range from a low concentration of 10 ppb (benzene) to 100 ppm (perfluoropropane). Performance testing is currently proceeding on the VCAM DU and LS units using the chemical cocktails generated from the 40 different species on the Priority 1, 2, and 3 lists. These tests are structured to confirm PCGC/MS performance and to mature the autonomous identification and quantification algorithms. The tests use a four- and six-point concentration variation to provide specific information on VCAM quantification accuracy and 24-hour repeatability. In addition to trace species detection capabilities VCAM units will quantify the three major atmospheric constituents N_2, O_2, and CO_2 in the cabin atmosphere. This provides dissimilar redundancy to the Major Constituents Analyzer already aboard ISS. The major constituent measurements will not use the PCGC system. Instead a sample of cabin atmosphere is directly introduced into the MS through a separate pulsed valve and conduction-limited tubing.

Shown in Figs. 4 and 5 (a-c) are a total ion

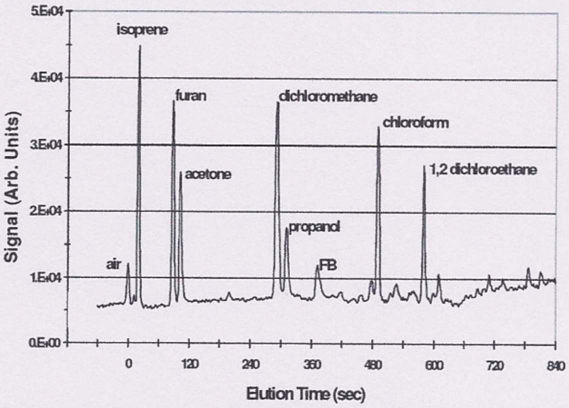

Figure 4. Total Ion Chromatogram for a Mixture of SMAC Species. The concentrations of isoprene, furan, dichloromethane, propanol, chloroform, and 1,2-dichloroethane are 24 ppb, 38 ppb, 30 ppb, and 31 ppb, respectively. PCGC conditions are: carrier gas at 15 psig, PC adsorb time of 6 min, GC temp isothermal at 25C for 320 sec then ramped to 85C at 5C/min. Acetone and FB are the calibration species. Propanol and the remaining unlabeled small elution peaks (< 10 ppb) are off-gassing products from the sample bag material.

chromatogram (Fig. 4) and the corresponding extracted mass fragmentation patterns for a mixture of SMAC species, obtained using the LS VCAM. The concentration of isoprene, furan, dichloromethane, chloroform, and 1,2-dichloroethane in these measurements was at or below the 180-day SMAC limit. Both the elution peak intensities and mass fractionation patterns are unambiguous, and VCAM software algorithms have had good success in autonomously identifying the species. The curves shown in Fig. 6 represent the VCAM signal response as a function of species concentration. These instrument response curves will be determined for each of the 40 target species and will be employed by the flight VCAM software for a more reliable and robust quantification. In VCAM testing to date instrument

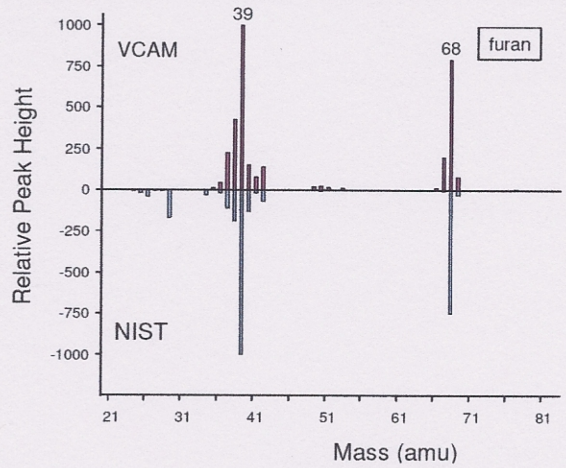

Figure 5b. Comparison of VCAM and NIST Mass Fragmentation Patterns for Furan. The top half of the plot represents the mass fragmentation pattern extracted from the elution peak labeled as furan in Fig. 4. The bottom half of the plot is the furan mass fragmentation pattern from the NIST database.

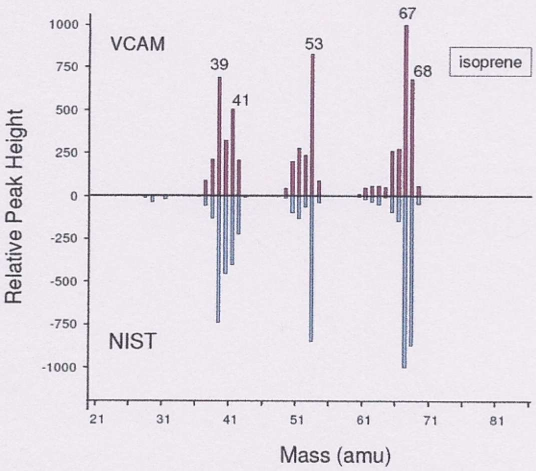

Figure 5a. Comparison of VCAM and NIST Mass Fragmentation Patterns for Isoprene. The top half of the plot represents the mass fragmentation pattern extracted from the elution peak labeled as isoprene in Fig. 4. The bottom half of the plot is the isoprene mass fragmentation pattern from the NIST database.

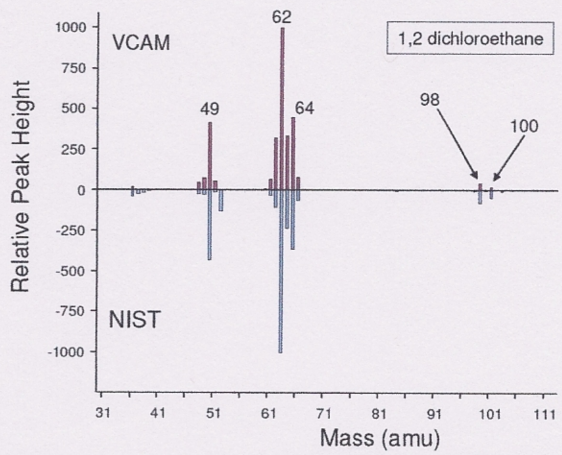

Figure 5c. Comparison of VCAM and NIST Mass Fragmentation Patterns for 1,2-Dichloroethane. The top half of the plot represents the mass fragmentation pattern extracted from the elution peak labeled as 1,2-dichloroethane in Fig. 4. The bottom half of the plot is the 1,2-dichloroethane mass fragmentation pattern from the NIST database.

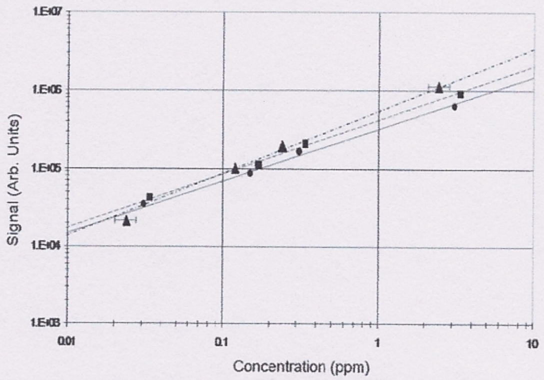

Figure 6. Variation of VCAM Signal as a Function of Concentration. The data represent the instrument response to isoprene (triangles, dot-dash line), 1,2-dichloroethane (circles, solid line), and furan (squares, dashed line). Error bars for the data points represent a combined 15% uncertainty in concentration generation and Poisson counting statistics.

sensitivity, selectivity, and reproducibility satisfy VCAM requirements.

The VCAM design includes calibration gases that will be used to validate and verify the following key operating parameters of VCAM while on-orbit: (1) the enhancement factor of the preconcentrator, (2) proper operation of the GC column by measuring the elution time and system sensitivity of the calibrant mixture, and (3) the mass range, mass resolution, mass cross talk, and system sensitivity of the Paul trap. Use will be made of a modified TO15 EPA Protocol for testing the instrument stability and response [6]. The TO15 protocol employs daily tests using fluorobenzene (FB, C_6H_5F, mass 96 amu) and bromofluorobenzene (BFB, C_6H_4FBr, mass 174 amu for the ^{79}Br isotope and 176 amu for the abundant ^{81}Br isotope acetone ($^{12}C_3H_6O$, 58 amu). For VCAM only FB and acetone ($^{12}C_3H_6O$) will be used to test the PCGC at the high- and low-mass ranges of the MS, respectively. VCAM ground-based testing suggests that once/week runs of the calibration gas mixture will be sufficient while on-orbit. Use of these calibrant gases in the closed ISS environment does not pose an astronaut health risk, even in the event of a total release.

CONCEPT OF OPERATIONS

VCAM is designed to autonomously sample and analyze the ISS cabin-air based upon an internal clock, astronaut front-panel commands, or *via* ground commands transmitted to ISS. VCAM baseline design is to operate once per day, with a nominal one-year life on orbit as limited by the helium carrier gas and calibration supplies. If longer-term operation is desired, these supplies are replaced as an orbital replacement unit (ORU) by the astronaut. This will extend the operational life by an additional year. It is expected that after installation in the EXPRESS rack VCAM will be commanded *via* gund interface, collecting performance and engineering data to confirm nominal operation in the ISS environment. Thereafter VCAM will perform autonomous measurements at a once-per-day frequency. All data will be deconvoluted and identified against an abbreviated and tailored NIST fractionation pattern library generated from VCAM verification testing. Concentrations are reported in mg/m^3. JPL and JSC scientists will have near-real time access to the VCAM health and status information *via* the TReK interface to HOSC. They will also have the ability to operate VCAM *via* a set of HOSC-vetted operational commands (*e.g.,* CLEAN, MEASURE AIR, IDLE) with the resultant raw data also down-linked in near-real time. In addition to the raw data the autonomously-determined identifications and concentrations will be down-linked to JSC through the health/status data link. The raw data (GC time-elution spectra and mass-fractionation spectra) will be used by JPL and JSC personnel during the initial ISS deployment phase for on-orbit validation. The communications link is an excellent resource that will allow for mitigation procedures and troubleshooting. For example, if an unknown species or an anomalous concentration of one species is detected the raw data will help confirm this result prior the astronauts' being alerted by ground personnel. VCAM will store all data, and downlink will occur when a communications link is available. Sufficient memory will reside in the VCAM to store up to 30 days' raw data.

FUTURE TECHNOLOGY DEVELOPMENTS

Typically the high quality *RF* voltage required for analytic mass spectrometers has been generated with bulky air-core transformers. For VCAM JPL eliminated the transformer and used a novel, digitally-generated numerically-controlled oscillator (NCO) for *RF* generation. The digital representation is filtered to reduce the presence of sidebands, and only the desired, main frequency is selected. The filtered output of the NCO is then amplified using conventional power amplifiers, and amplified further in the low-Q tank circuit containing the Paul trap capacitance. Shown in Fig. 7 is the VCAM mass spectrometer controller card that contains the circuitry for RF generation, multichannel scaling of the CEM output, and MS

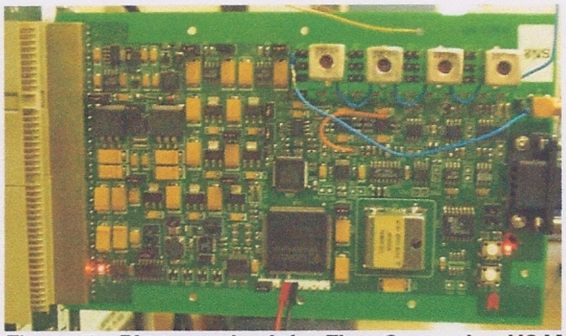

Figure 7. Photograph of the First Generation VCAM Direct Digital *RF* Synthesis Board. The circuitry generates the ~500kHz *RF* drive voltage for the MS, multichannel scaling of the CEM outputs, and generates the MS timing pulses. The card is 3"x 6" and consumes ~ 8W at 28Vdc

timing-pulse generation [7]. The card affords significant reduction in mass, volume, and power over previous MS electronics. Further reductions are in progress at JPL by implementing a credit-card size chip-based *RF* electronics package. Testing on this new device is planned to commence in 7/08. Testing is also underway with high efficiency robust ionizers based on patterned carbon-nanotube arrays.

SUMMARY AND CONCLUSIONS

The VCAM GC/MS in operation has demonstrated the ability to detect and quantify complex mixtures of the ISS SMAC target chemicals. To date, this represents the best implementation of terrestrial "gold standard" GC/MS instrumentation into an LDHF environment. Testing has shown that the temporal separation in the GC column coupled with the high specificity of the mass spectrometer is allows for unambiguous compound identifi-cation. The MS sensitivity and resolution required to measure each analyte's mass fractionation pattern ("fingerprint") are excellent. VCAM is modular in design, both in terms of accommodating new features, such as a water-extraction module; and in terms of miniaturization, by allowing replacement of board-size power supplies, amplifiers and NCOs with chip-size equivalents as they become available. These technology advances greatly enhance the amenability of the PCGC/MS to use in the varied environments of NASA's future LDHF and robotic planetary missions.

ACKNOWLEDGMENTS

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LIST OF ACRONYMS

DU: Development Unit
EPA: Environmental Protection Agency
GC/MS: Gas Chromatograph/Mass Spectrometer
HOSC: Huntsville Operations Support Center
ISS: International Space Station
LS: Laboratory Standard
LDHF: Long Duration Human Spaceflight
MCE: Monitor and Control Electronics
NCO: Numerically-Controlled Oscillator
NIST: National Institute of Standards and Technology
ORU: Orbital Replacement Unit
PC: Preconcentrator
PE: Processor Electronics
RF: Radiofrequency
SMAC: Spacecraft Maximum Allowable Concentration
TReK: Telescience Research Kit
VCAM: Vehicle Cabin Atmosphere Monitor